

JUL 15 1959 RECEIVED

Paper for 1959 ASLE-ASME Lubrication Conference
Sheraton-McAlpin Hotel
New York City
October 20-22, 1959

-no dup

THE INFLUENCE OF SILICON ADDITIONS ON FRICTION AND WEAR

OF NICKEL ALLOYS AT TEMPERATURES TO 1000° F

By Donald H. Buckley and Robert L. Johnson

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio

N 65-85335

Code page

msa TMX 56489

ABSTRACT

Small additions of silicon have considerable beneficial effect on performance on slider alloys. This effect has usually been attributed to increased hardness. The research reported was conducted to consider a hypothesis that the primary role of silicon in slider alloys is one of supporting the formation of protective surface films.

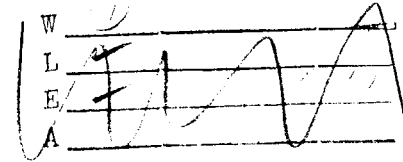
Friction and wear data were obtained at temperatures from 75° to 1000° F with a series of binary silicon-nickel alloys containing up to 10 percent silicon. Pertinent hot hardness, metallurgical and surface-film analysis data are included. Atmospheres used were air, mixtures of oxygen and argon, a mixture of hydrogen and nitrogen, and a halogenated methane gas lubricant.

The results show the role of silicon as a film former to be of great importance in success of silicon-containing alloys as slider materials for extreme temperatures. The range of variables studied gave friction coefficients from 0.05 to >10.00 depending on film formation tendencies. Alloys with 5 percent or more silicon having a duplex structure showed the best results. Film formation resulted from surface reactions or the smearing of the softer phase from the alloys having duplex structure.

u,

copy

TMX# 56 489



INTRODUCTION

Extremely high temperatures (e.g., 1000° F) must be anticipated for lubricated parts in future powerplants of aerodynamic and space vehicles. Many factors important in high-temperature lubrication require careful study including the interaction of the atmospheres, the lubricants, and the metals for lubrication. In this paper primary consideration is given to the influence of one alloy constituent, silicon, on the performance of metals for lubrication.

Numerous instances are reported in the literature where the presence of a small amount of silicon in bearing metals has contributed to successful operation. The reasons why silicon additions have been helpful are not clear. It has usually been suggested that silicon additions improve bearing alloys because of increased hardness (refs. 1 and 2). Hardness alone is not the answer, however, because hardness, per se, gained by other methods will not give similar benefits. Various investigators have indicated that surfaces of bearing alloys containing silicon show evidence of glazes (ref. 3). NASA experience with nickel-, and copper-, and iron-base alloys containing silicon has also shown (refs. 4 and 5) the importance of films that could be glazes. In complex alloys it is difficult to assign responsibility for a common observed phenomenon, such as glazing, to one of the many constituents.

Silicon in metals reasonably can be expected to have a surface film effect that is out of proportion to its concentration in the alloy. Reference 6 indicates that, as surface films of oxides are formed on metals, the concentration of the refractory oxide such as SiO_2 may be four times that represented by the amount of metal (silicon) in the composition of

the base alloy. With highly alloyed compositions of steel, the oxide layers adjacent to the metal may consist entirely of the refractory oxide.

The common observation of surface glazes with alloys containing silicon may be explained by two facts. First, elemental silicon is extremely reactive with oxidizers and, in practice, it is perhaps more widely used as an oxygen "getter" in alloys than for any other single purpose. Second, SiO_2 is one of the most common and effective vitrification agents for glass (ref. 7).

The glazes formed on slider surfaces are amorphous films that are probably of eutectic compositions. Since low melting point is usually associated with low shear strength (ref. 8), it is likely that surface shear occurs in the glaze film rather than in the metals or in the substrate oxides. This condition is conducive to low wear. By broadening the temperature range for softening, of surface glazes a vitrification agent can contribute to low friction. Thus, viscous shear may be obtained in the surface layer over a substantial range of experimental lubrication conditions.

The objective of this research was to clarify experimentally the role of silicon in slider alloys by evaluating the importance of the film formation concept described previously. The experiments were simplified by using specially cast binary silicon-nickel alloys with varied amounts of silicon up to 10 percent. Nickel alloys are of particular interest because they can be used in extreme temperature lubrication with gases such as CF_2Br_2 (ref. 9). To evaluate the role of surface reaction films, data were obtained in a reducing gas, in gases containing varied amounts

of oxygen, and in a halogen-substituted methane. Friction and wear data were obtained with a 3/16-inch-radius hemisphere sliding on the flat surface of a rotating disk; the load was 1200 grams, ambient temperatures were from 75° to 1000° F, and the sliding velocity was 120 feet per minute.

MATERIALS

The friction and wear test specimens used in this investigation were Inconel-X (70 Ni, 15 Cr, 5-9 Fe, plus traces of Si, C, Mn, S, Al, Cb.) L-nickel (99.4 Ni with especially low carbon) and four silicon-nickel alloys of various silicon contents: 2.5, percent, 5.0 percent, 7.5 percent, and 10.0 percent. In all experiments the disk and rider were of the same material. The binary silicon-nickel alloys were prepared at the Lewis Research Center by the addition of the necessary percent of silicon to 3-pound heats of L-nickel. The L-nickel was held at a temperature of 2750° F and the silicon was added. The molten alloy was then centrifugally cast in molds at a temperature of 1600° F. The alloy was then cooled in the mold to room temperature. The same procedure was followed for all compositions. Since the alloy preparation was not accomplished in a vacuum furnace it is anticipated that a small portion of the silicon oxidized to form silicon dioxide (SiO_2) and existed in the structure as such. The SiO_2 would be stable under all the conditions of these experiments including the reducing atmosphere. In the reducing atmosphere a temperature in excess of 2000° F would be needed to reduce the SiO_2 .

The phase diagram for the silicon-nickel system (ref. 10) indicates that two phases exist within the range of 0 to 10 percent silicon. The first or α -phase is essentially a solid solution of silicon in nickel and exists in alloys from 0 to 5 percent silicon. From 5 to approximately 12

percent silicon, a new phase is formed at the grain boundaries. This second or β -phase is the compound Ni_3Si (see figs. 2(a) to (d), ref. 10). The 7.5 percent silicon-nickel (fig. 2(c)) had cored (variable solid solution) areas as indicated. These areas could have been reduced in size by holding the alloy at solution temperature for a prolonged period; however, it is doubtful that they could be eliminated completely. A commercial grade 7.5-percent-silicon nickel had cored areas and a metallurgical structure almost identical to the alloy prepared at Lewis Research Center.

Hardness data for the metals used in this study are presented in table I. In addition, to the standard Rockwell hardness, Knoop microhardness, and hot hardness data were obtained. The Knoop microhardness indentations for the 2.5 percent, 5.0 percent, 7.5 percent, and 10 percent silicon-nickel are shown in the photomicrographs of figures 1(a) through (d). The hot hardness data were obtained with a modified Rockwell superficial hardness tester at temperatures of 600° and 1000° F. The method for hot hardness testing was adapted from that of reference 10.

The gases used in this investigation were: air, 7 percent oxygen in 93 percent argon, 40 percent oxygen in 60 percent argon, (7 percent hydrogen (H_2) in 93 percent nitrogen (N_2) (forming gas), and dibromodifluoromethane (CF_2Br_2).

APPARATUS

The apparatus used in this investigation is described in detail in reference 9 and is shown schematically in figure 2. The basic elements of the apparatus consist of a rotating disk specimen ($2\frac{1}{2}$ -in. diam.) and a hemispherically tipped rider specimen ($3/16$ -in. rad.).

The rider specimen is stationary and in sliding contact with the rotating disk specimen. The disk was rotated by means of an electric motor through a variable speed transmission. Loads were applied to the rider specimen by means of a dead weight system. The frictional force was measured directly by means of four strain gages mounted on a copper-beryllium dynamometer ring. The frictional force was continuously recorded on a strip chart potentiometer. After the experiment, the wear volume was calculated from the measured diameter of the wear area on the rider specimen.

The gases were introduced into a 2-liter Inconel test chamber which enclosed the disk and rider specimen. The test chamber was heated by means of strip heaters mounted on the outer walls and concentric ring heaters in the chamber base. The temperature was measured by an Inconel-sheathed Chromel-Alumel thermocouple located along the side of the disk specimen. The temperatures were varied from 75° to 1000° F.

PROCEDURE

The rider and disk specimens were finish ground to 2 to 4 micro-inches. Prior to experiments the rider and disk were given the same preparatory treatment, which consisted of the following: (1) a thorough rinsing with acetone to remove oil and grease from the surface, (2) polishing with moist levigated alumina and a soft polishing cloth, (3) the specimens were thoroughly rinsed in tap water followed by distilled water, and (4) the specimens were rinsed with absolute ethyl alcohol and finally with C.P. acetone to remove any trace of water.

The details on the system of transfer of gases to the test chamber are presented in reference 9. The test chamber was purged for a 15-minute period prior to starting the run. The gas-flow rates and mixtures used in the purge were the same as those employed in the run. At the completion of the purge the run-in procedure was initiated.

The run in was started with an initial surface speed of 55 feet per minute and incremental loads of 200, 400, and 600 grams applied in 1-minute intervals. A 1200-gram load was then applied for a period of 2 minutes at the end of which time the surface speed was increased to 120 feet per minute. This speed was maintained for the duration of the 60-minute run.

The run-in procedure was found necessary as a result of some previous work with lubricating gases, which showed that if the run was started with high load and speed, surface failure of the specimens was apt to occur. The inadequate lubrication was attributed to the lack of sufficient time for the formation of a reaction film. Careful run in employing reduced speed and incremental loading, formed an adequate reaction film, which markedly reduced the initial high friction and wear.

RESULTS AND DISCUSSION

References 1 and 2, as well as other sources, have suggested that silicon is important in slider alloys because it increases hardness. Two nickel-base materials of approximately equal hardness were run in order to learn if other factors were also important. Inconel-X contains only trace amounts of silicon and is of hardness equivalent to 7.5 percent silicon-nickel (table I). Results obtained in experimental runs at 75 to 1000° F with these two alloys are presented in figure 3. The friction

coefficient for the 7.5 percent silicon-nickel (0.5) was much less than for the Inconel-X (0.8) over the entire temperature range; the wear was one-third of that for Inconel-X. The differences in friction and wear of the two-nickel-base alloys was caused by some factor other than hardness such as film formation properties.

A further examination of the influence of silicon was made with a 2.5 percent silicon-nickel alloy. A 2.5 percent silicon-nickel was used because it was a single phase alloy and thus could be compared with L-nickel and Inconel-X. Friction and wear experiments were conducted with the alloy in air and in a reducing atmosphere at 75^o, 600^o, and 1000^o F. The results are presented in figure 4. In air, the coefficient of friction for the 2.5 percent silicon-nickel decreased with increasing temperatures. Increasing temperatures also decreased the hot hardness (table I) and probably decreased the shear strength of the metal. Friction fundamentals would suggest that the influence of decreasing hot hardness alone would be to increase the friction coefficient ($f = S/H$, ref. 8). The influence of decreasing hardness combined with decreasing shear strength might be to give essentially constant friction coefficient with increasing temperatures. Neither result was observed. The observed behavior showed decrease in friction and wear with increasing temperature, greater friction in a reducing atmosphere than in air, and extreme differences in wear (two orders of magnitude) in air and in the reducing atmosphere at 1000^o F. These observations emphasize the importance of surface reaction films. A reaction film can give a reduction in the shear term that would be proportionally greater than the reduction in hardness with increasing temperatures.

A comparison of data obtained in air and a reducing atmosphere indicates greater friction and wear for 2.5 percent silicon-nickel in forming gas where surface film formation was not possible. As mentioned earlier, residual SiO_2 formed during casting was probably present and could have a beneficial influence in the reducing atmosphere. X-ray diffraction analysis of the wear debris from the 2-5 percent silicon-nickel run in air at 1000°F indicated the composition of the debris to be essentially silicon dioxide (SiO_2) and metallic nickel; alloys with more silicon had wear debris that gave diffuse patterns indicating amorphous material.

Room temperature data. - Friction and wear data were obtained in various gas atmospheres for silicon-nickel alloys containing from 0 to 10 percent silicon. The friction results are presented in figure 5. The friction coefficient for L-nickel in a reducing atmosphere was extremely high (>10.0). The specimens seized and the run had to be stopped to prevent damage to the apparatus. The additions of silicon in the nickel alloys resulted in significant reduction in friction coefficient even in the absence of oxygen. The presence of residual SiO_2 in the alloys could have influenced the result.

In experiments conducted in oxygen-containing atmospheres (air, 40 percent O_2 in argon, and 7 percent O_2 in argon) the friction coefficient decreased with increasing percentage of silicon. Varying the oxygen content of the atmosphere from 7 to 40 percent had very little influence on the results obtained.

The gas CF_2Br_2 has a boiling point of 76°F and in the friction experiments at room temperature the gas condensed on the test specimens, resulting in essentially boundary lubrication by liquid. The friction coefficient at room temperature therefore did not reflect the influence of silicon. Much

lower friction and wear were obtained in CF_2Br_2 than in any of the other atmospheres.

The wear of the rider specimen was extremely high for L-nickel in all atmospheres (fig. 6). As the percentage of silicon increased the wear decreased. With silicon content above 5 percent, the wear was relatively constant with no significant difference regardless of atmosphere.

600° F Data. - Friction and wear were data obtained in various gas atmospheres for silicon-nickel alloys at 600° F. In general, the friction coefficient at 600° F (fig. 7) was lower for all atmospheres and silicon percentages than the values obtained at room temperature. Results obtained in air and forming gas were similar. The friction coefficients were in the range of good boundary lubrication.

Wear at 600° F (fig. 8) was lower than at room temperature for the 2.5 percent silicon nickel. With CF_2Br_2 gas, wear was extremely low for all silicon-containing alloys as well as for the L-nickel.

1000° F Data. - In general, at 1000° F the friction decreased with increasing percentage of silicon in both reducing and oxidizing atmospheres (fig. 9). An increase in silicon content from 2.5 percent to 5.0 percent results in a marked decrease in friction (1.0 to 0.6). This decrease can be related to the change in alloy structure, from a single phase to a duplex structure. The friction was very low ($f = <0.1$) with CF_2Br_2 for all compositions and equivalent to effective boundary lubrication.

The wear results (fig. 10) indicate that even relatively small additions of silicon to nickel markedly reduce the wear in an oxygen-containing atmosphere at 1000° F. The 2.5 percent silicon-nickel had nearly the same

hardness as L-nickel at 1000^o F. The wear of L-nickel was so catastrophic as to prevent reasonable wear measurement; it was, however, many times that measured for 2.5 percent silicon-nickel. The wear with the 5.0, 7.5, and 10 percent silicon-nickel alloys was insignificant compared with that obtained with L-nickel and 2.5 percent silicon nickel in the reducing atmosphere at 1000^o F.

The significant reduction in wear observed with higher silicon-containing alloys is due to the duplex structure of the alloys. The duplex structure consists essentially of two alloy phases, one that is relatively soft (the α phase) and one that is relatively hard (the β phase). The softer phase appears to be smeared over the harder (fig. 12(b)). The wear data obtained in CF₂Br₂ was lower for all alloys containing silicon, as well as for L-nickel, than that obtained in any other atmosphere. The low wear rate was due to the effectiveness of the halides formed as boundary lubricants.

Discussion of mechanism. - The concept (refs. 1 and 2) that increased hardness accounts for the good friction and wear properties of silicon-containing alloys is not adequate to explain the results reported herein. The data obtained with Inconel-X and 7.5 percent silicon-nickel should be noted especially. Although the two materials had similar hardness the 7.5 percent silicon-nickel gave much lower friction and wear than the Inconel-X at all temperatures investigated. Further, data obtained with L-nickel and 2.5 percent silicon-nickel in air at 1000^o F, where both materials possess the same hardness, indicated marked differences in friction and wear. Figures 10 and 11 show that the wear was substantially lower for the 2.5 percent silicon-nickel than for L-nickel.

The improved friction and wear properties of alloys containing silicon may be attributed to the strong affinity of silicon for oxidants at high temperatures. The oxidation of silicon can result in the formation of such compounds as silicon dioxide (SiO_2) or silicon tetrabromide (SiBr_4). A compound such as SiO_2 may combine with the low metal oxides or function alone in forming a surface glaze. The surface glaze serves to reduce friction and wear. This effect is indicated in figure 12(a) where preferential oxide formation builds up in the silicon-rich areas of the grain boundaries. No similar surface was observed with specimens run in forming gas (fig. 12(b)).

In a halogen containing atmosphere, a somewhat similar result was obtained. With the bromine containing gas, CF_2Br_2 , the reaction product with the silicon of the alloy was essentially silicon tetrabromide. The preferential reaction of the bromine with the silicon-rich areas is indicated in figure 12(c). This effect was not observed in the forming gas atmosphere.

The mechanism believed responsible for the relatively low friction and wear values obtained with 5.0 percent, 7.5 percent, and 10 percent silicon nickel in forming gas was dependent upon the duplex structure of these alloys. The mechanism here is physical rather than chemical, as postulated in the introduction. The relatively soft α phase (silicon-nickel solid solution) is smeared across the harder β phase (Ni_3Si) resulting in relatively low friction and wear. This same mechanism has been observed in unreported work done at NASA with cemented carbides, where the softer binder material was smeared over the hard carbide surface. This same mechanism might well function in other atmospheres where the reaction of silicon is insufficient to provide a surface glaze. It must be noted, however, that under conditions

where it remains a stable compound the residual SiO_2 formed in casting may be important to the slider behavior.

SUMMARY OF RESULTS

A study was made of the effect various percentages of silicon additions had on the friction and wear properties of nickel. Experiments were conducted in various gas atmospheres at temperatures up to 1000°F . The following observations were made:

1. Surface reaction films formed in oxidizing atmospheres (containing oxygen or bromine) are formed more readily with nickel alloys containing silicon. Formation of reaction films is accelerated by elevated temperatures. These surface films serve to reduce friction and wear.

2. A soft-phase surface flow mechanism was observed. This mechanism was of predominant importance in a reducing atmosphere. Nickel-silicon alloys containing 5 to 10 percent silicon have a duplex structure; during sliding, surface flow of the softer α -phase (Si-Ni solid solution) over the harder β -phase (Ni_3Si) provides a protective surface film.

REFERENCES

1. Kozlik, R. A.: Wear and Frictional Characteristics of Some Nickel-Base Alloys Tested at Room Temperature. The International Nickel Company Bull. IM 8-57, 3421, pp. 6-7.
2. Mataich, P. F., and Wagner, C. F.: Retainer Materials for Aircraft Gas-Turbine Bearings. TR 56-294, WADC, Aug. 1956, pp. 12-13. (AD-97235.)
3. Burwell, J. T.: Mechanical Wear. Am. Soc. for Metals, Jan. 1950, pp. 241-258.

4. Johnson, R. L., Swikert, M. A., and Bisson, E. E.: Wear and Sliding Friction Properties of Nickel Alloys Suited for Cages of High Temperature Rolling-Contact Bearings. I - Alloys Retaining Mechanical Properties to 600⁰ F. NACA TN 2758, 1952, pp. 5-12.
5. Johnson, R. L., Swikert, M. A., and Bisson, E. E.: Wear and Sliding Friction Properties of Nickel Alloys Suited for Cages of High Temperature Rolling-Contact Bearings. II - Alloys Retaining Mechanical Properties above 600⁰ F. NACA TN 2759, 1952, pp. 5-12.
6. Clark, F. H.: Metals at High Temperatures. Rheinhold Pub. Corp., 1950, p. 345.
7. Morey, G. W.: The Properties of Glass. Rheinhold Pub. Corp., 1938, p. 75.
8. Merchant, M. E., and Ernst, H.: Conference on Friction and Surface Finish. MIT, 1940, p. 76.
9. Buckley, D. H., and Johnson, R. L.: Halogen-Containing Gases as Boundary Lubricants for Corrosion-Resistant Alloys at 1200⁰ F. NASA MEMO 2-25-59E, 1959, p. 7.
10. Metals Handbook 1948, ed.: Am. Soc. of Metals, Cleveland, Ohio.

FIGURE TITLES

- Fig. 1. - Diagram of friction apparatus.
- Fig. 2. - Photomicrographs (250 X) of silicon-nickel alloys.
- Fig. 3. - Friction and wear of 2.5 percent silicon-nickel on 2.5 percent silicon-nickel in air and a reducing gas.
- Fig. 4. - Friction and wear of 7.5 percent silicon-
- Fig. 5. - Coefficient of friction for silicon-nickel alloys in various gases at room temperature.
- Fig. 6. - Wear of silicon-nickel alloys in various gases at room temperature.
- Fig. 7. - Coefficient of friction for silicon-nickel alloys in various gases at 600° F.
- Fig. 8. - Wear of silicon-nickel alloys in various gases at 600° F.
- Fig. 9. - Coefficient of friction for silicon-nickel alloys in various gases at 1000° F.
- Fig. 10. - Wear of silicon-nickel alloys in various gases at 1000° F.
- Fig. 11. - Photomicrographs (15 X) of the wear on L-nickel and 2.5 percent silicon-nickel rider specimens.
- Fig. 12. - Photomicrographs (15 X) of wear tracks on 10 percent silicon-nickel disk specimen run in various gases at 1000° F.

TABLE I. - HARDNESS DATA

Alloy composition	Area	Standard Rockwell	Knoop microhardness		Rockwell superficial hardness		
			Room temperature		Room temperature	600° F	1000° F
			Knoop scale	Conversion to Rockwell			
L-Nickel	Normal surface	R _B 45-65			R _B 61	R _B 9	R _B 1
	Wear track				R _B 68		
2.5 Percent silicon-nickel	Normal surface	R _B 69	KHN 138	R _B 69	R _B 63	R _B 8	R _B 4
	Wear track				R _B 68		
5.0 Percent silicon-nickel	Normal surface	R _B 84		R	R _B 84	R _B 33	R _B 33
	α-phase ^a β-phase ^b		KHN 138 KHN 265	R _B 69 R _C 23			
7.5 Percent silicon-nickel	Normal surface	R _C 30			R _C 30	R _C 30	R _B 94
	α-phase ^a β-phase ^b Cored area		KHN 360 KHN 677 KHN 215	R _C 36 R _C 59 R _B 93			
10.0 Percent silicon-nickel	Normal surface	R _C 41			R _C 41 av. (31-51)	R _C 41 av. (21-61)	R _C 31 av. (4-61)
	α-phase ^a β-phase ^b		KHN 384 KHN 677	R _C 38 R _C 59			
Inconel-X	Normal surface	R _C 29			R _C 29	R _C 27	R _C 23

^aα-phase - represents solid solution of silicon in nickel^bβ-phase - Ni₃Si compound.

DIAGRAM OF FRICTION APPARATUS

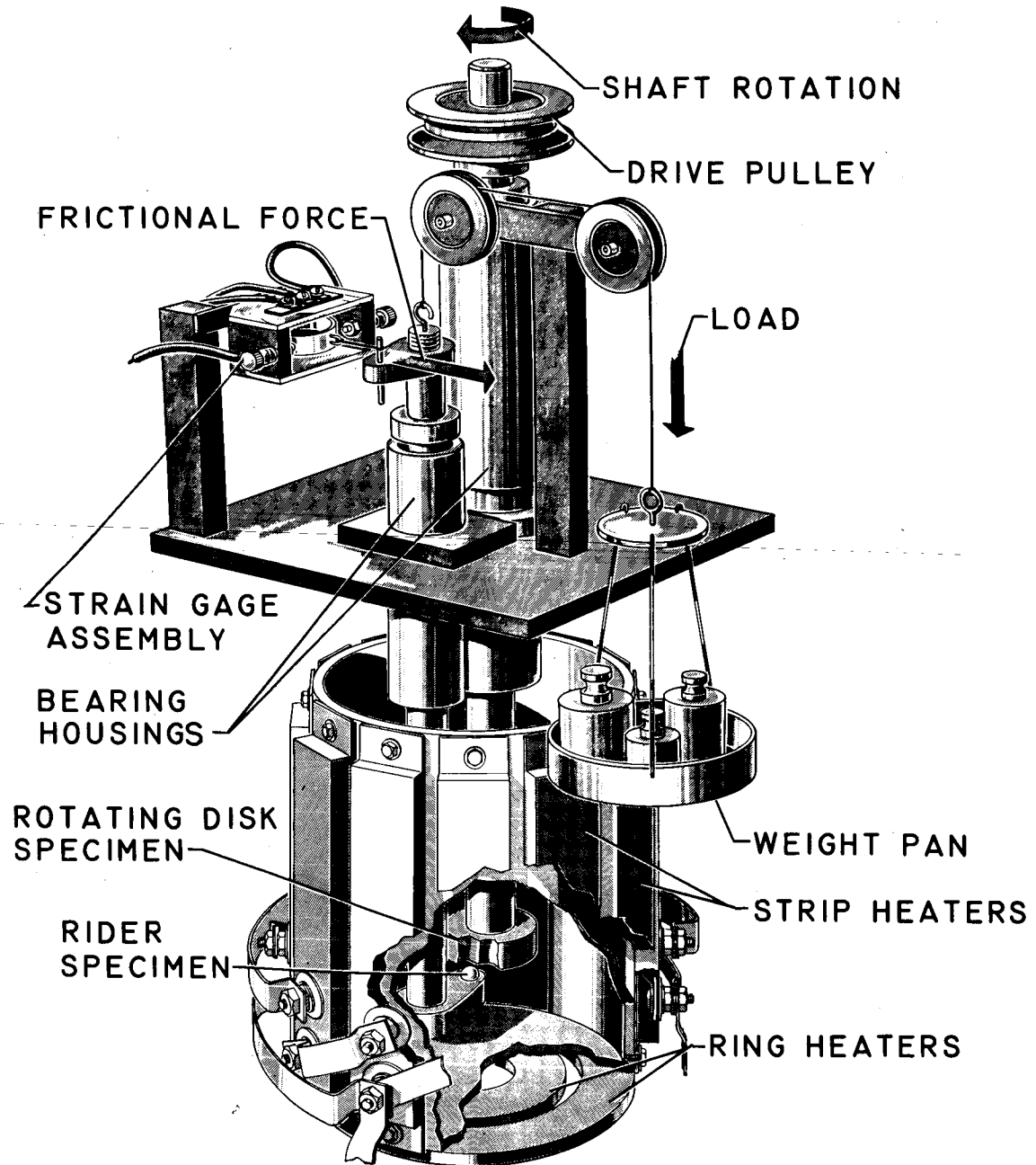


Figure 1.

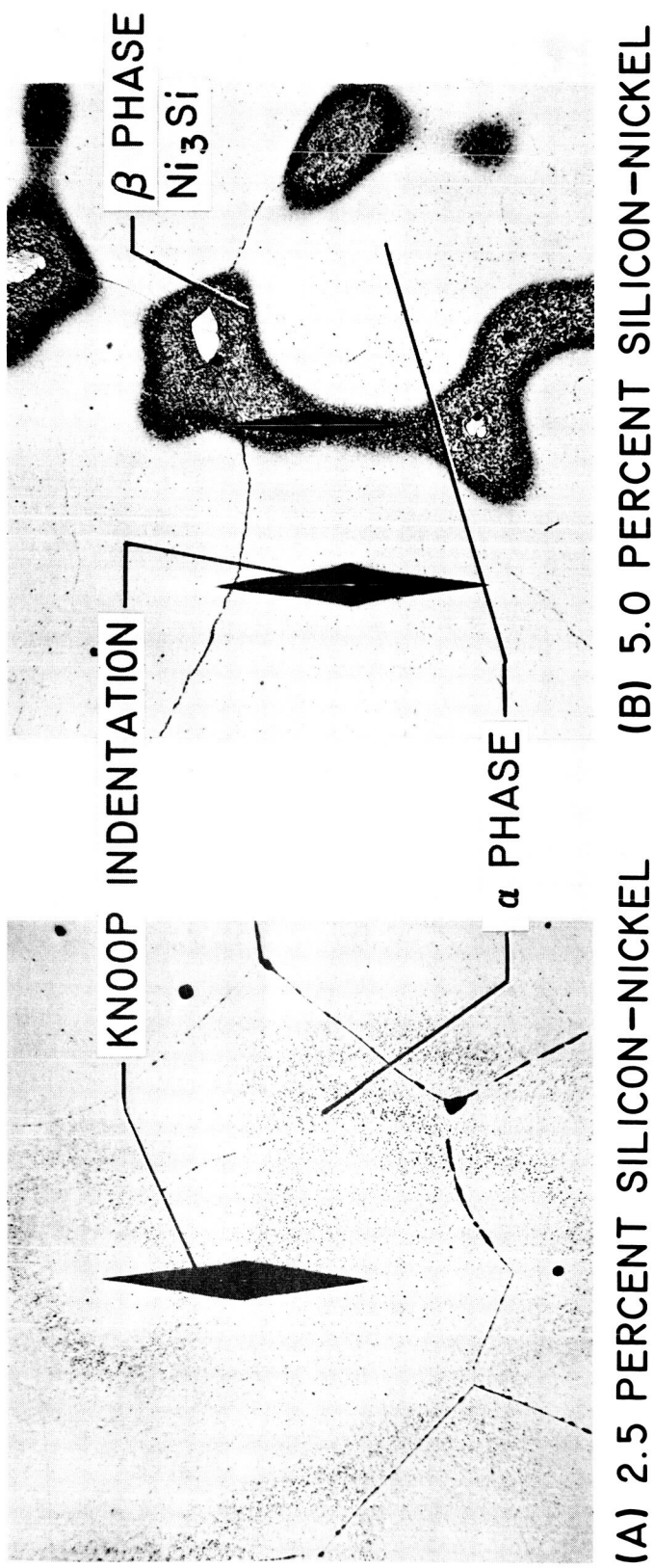
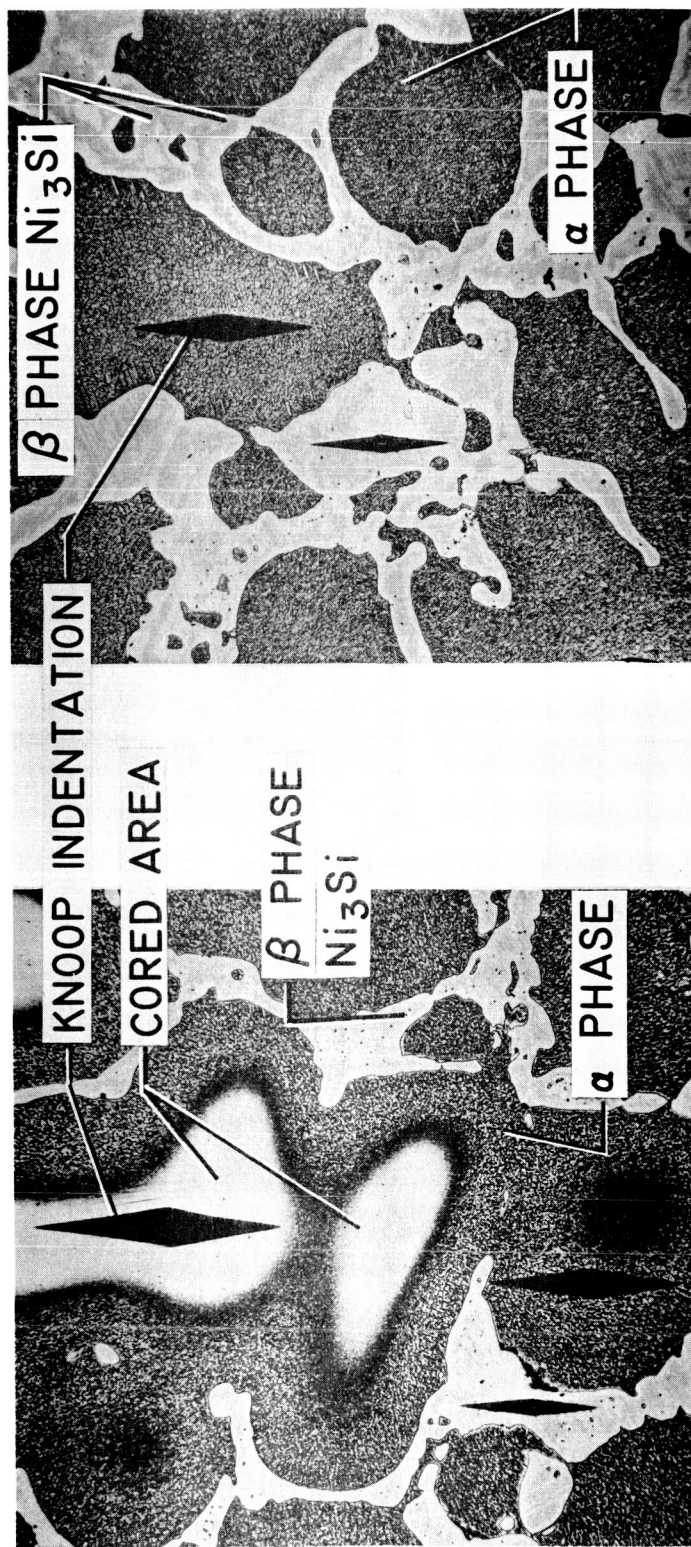


Figure 2.



(C) 7.5 PERCENT SILICON-NICKEL (D) 10.0 PERCENT SILICON-NICKEL

Figure 2. - Concluded.

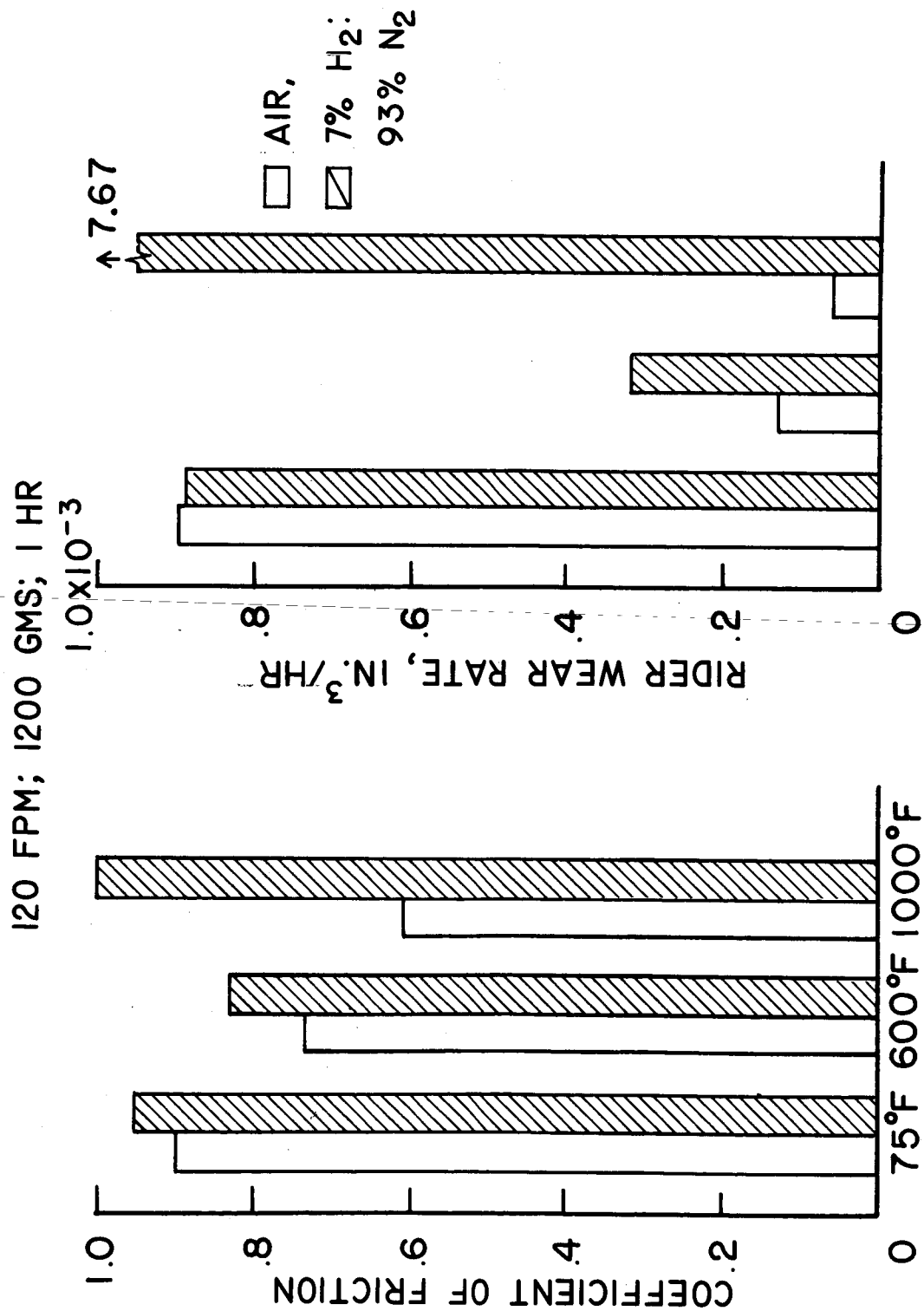


Figure 3.

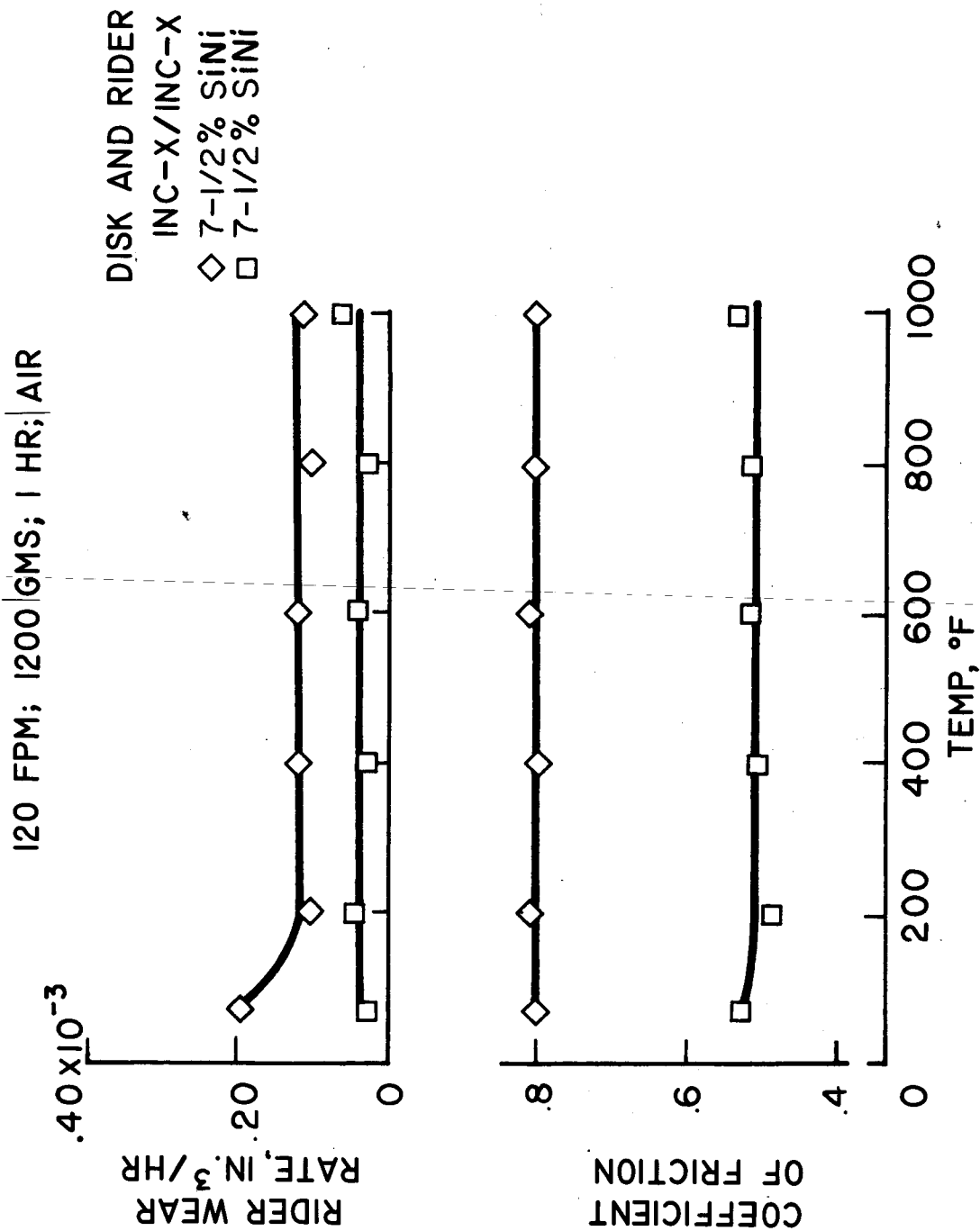


Figure 4.

120 FPM; 1200 GMS; 1 HR

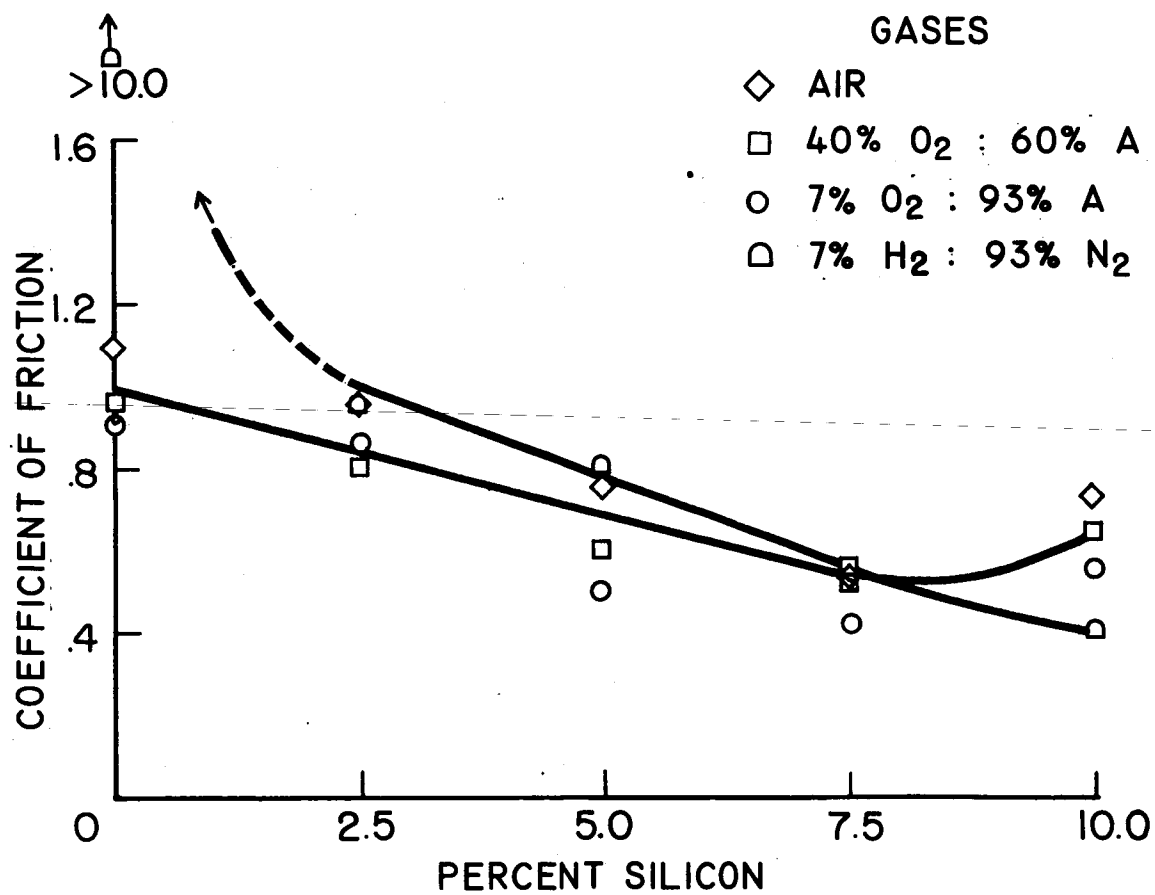


Figure 5.

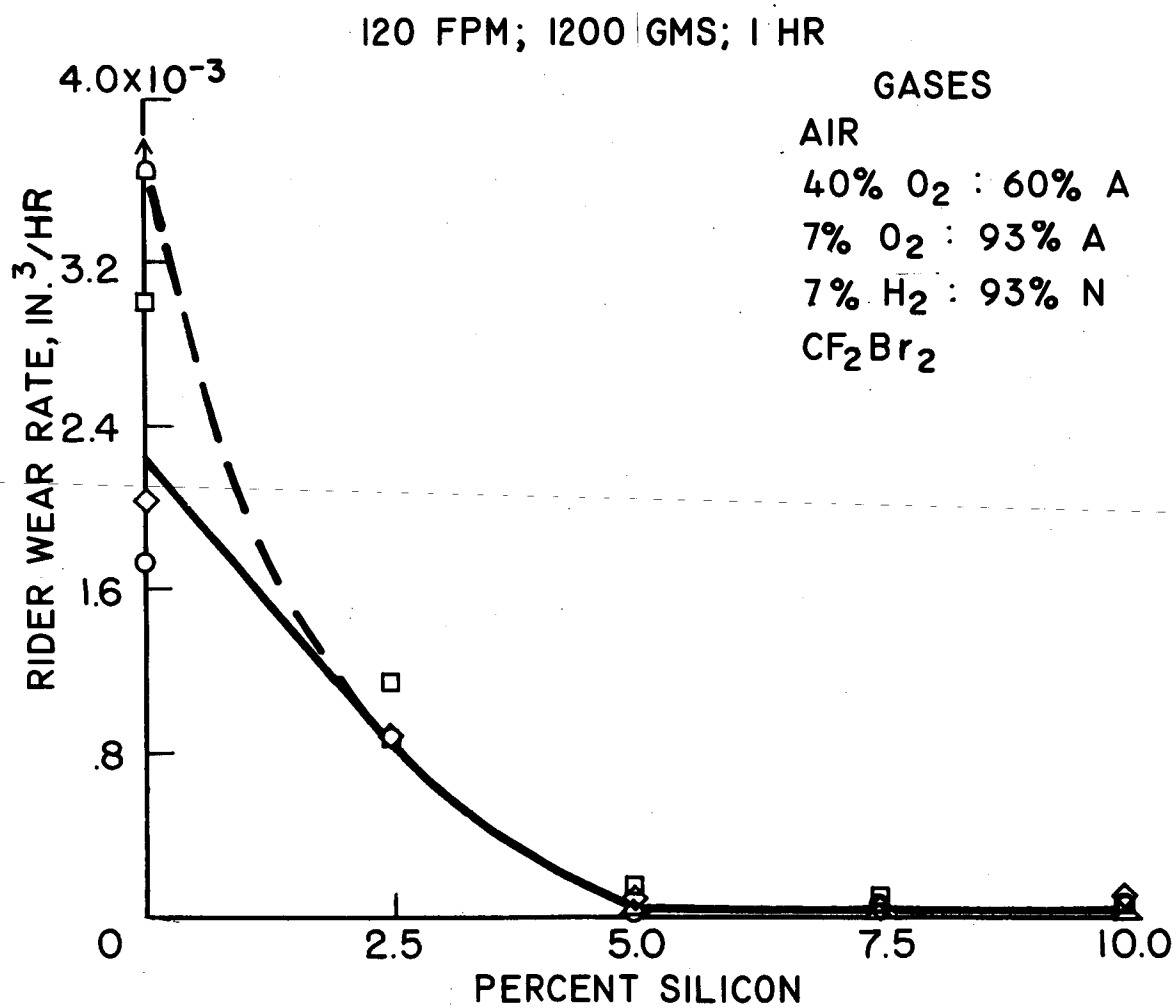


Figure 6.

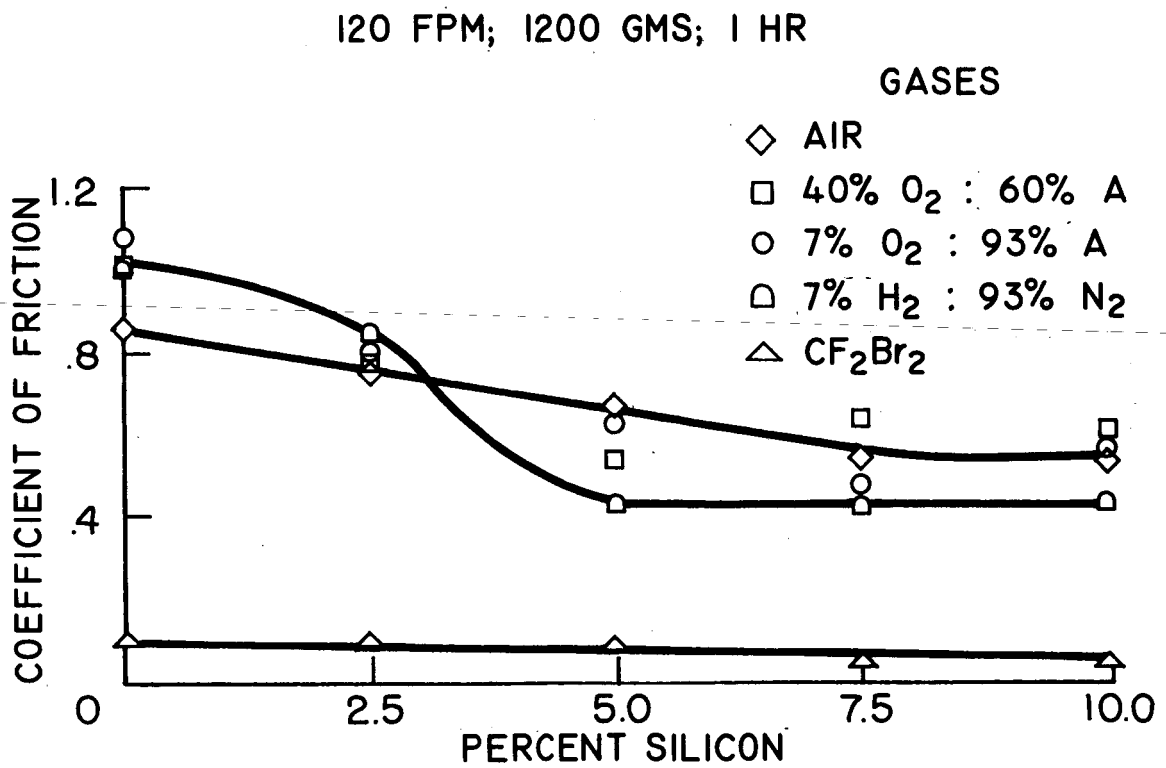


Figure 7.

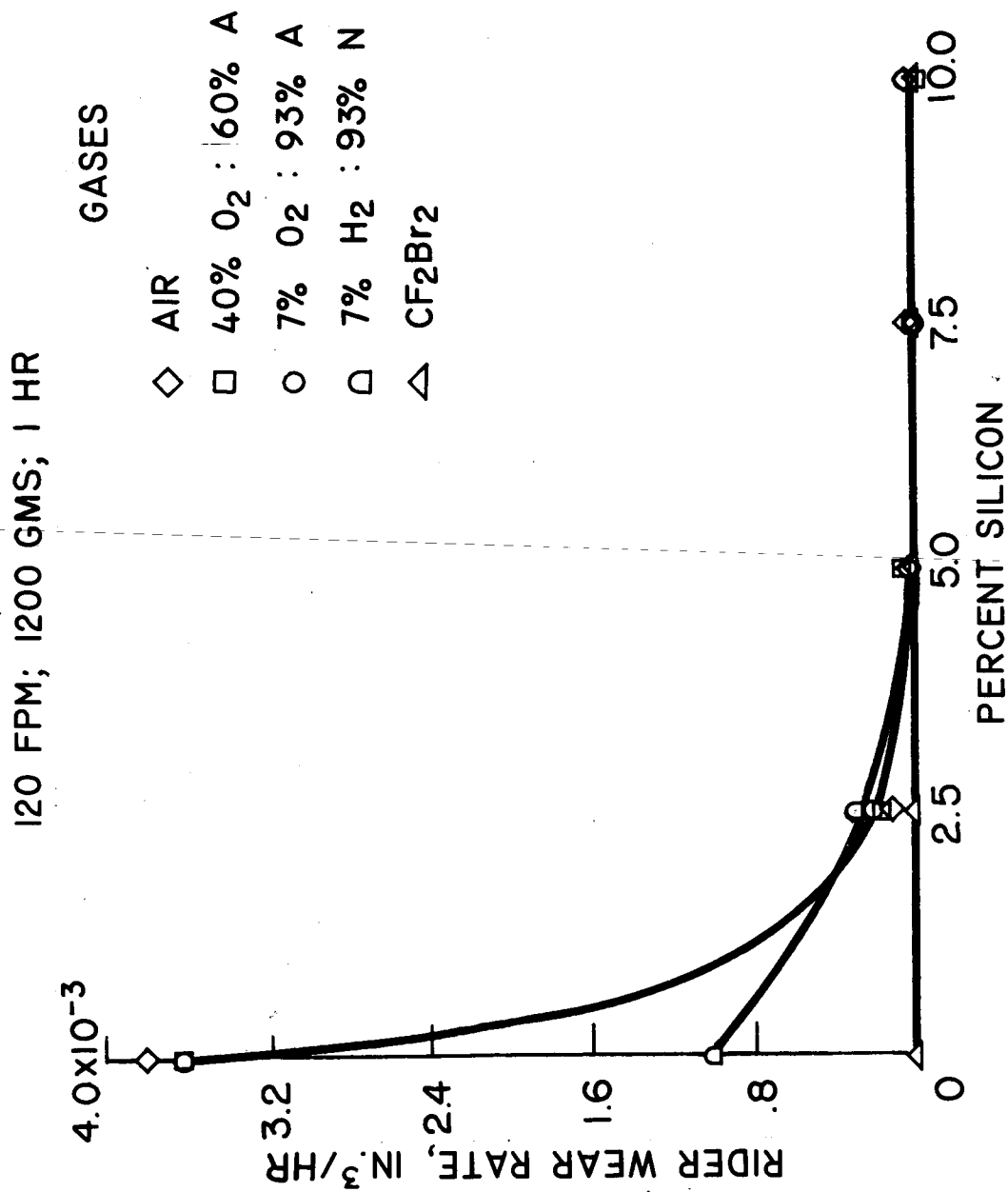


Figure 8.

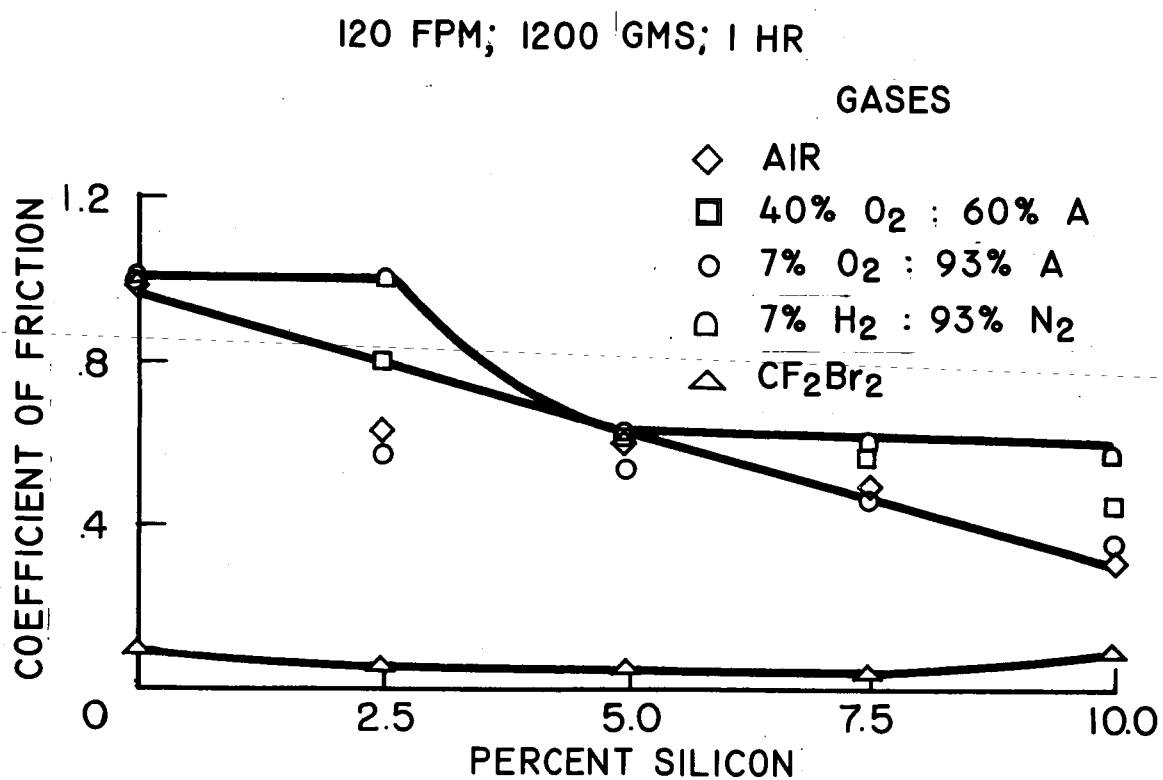


Figure 9.

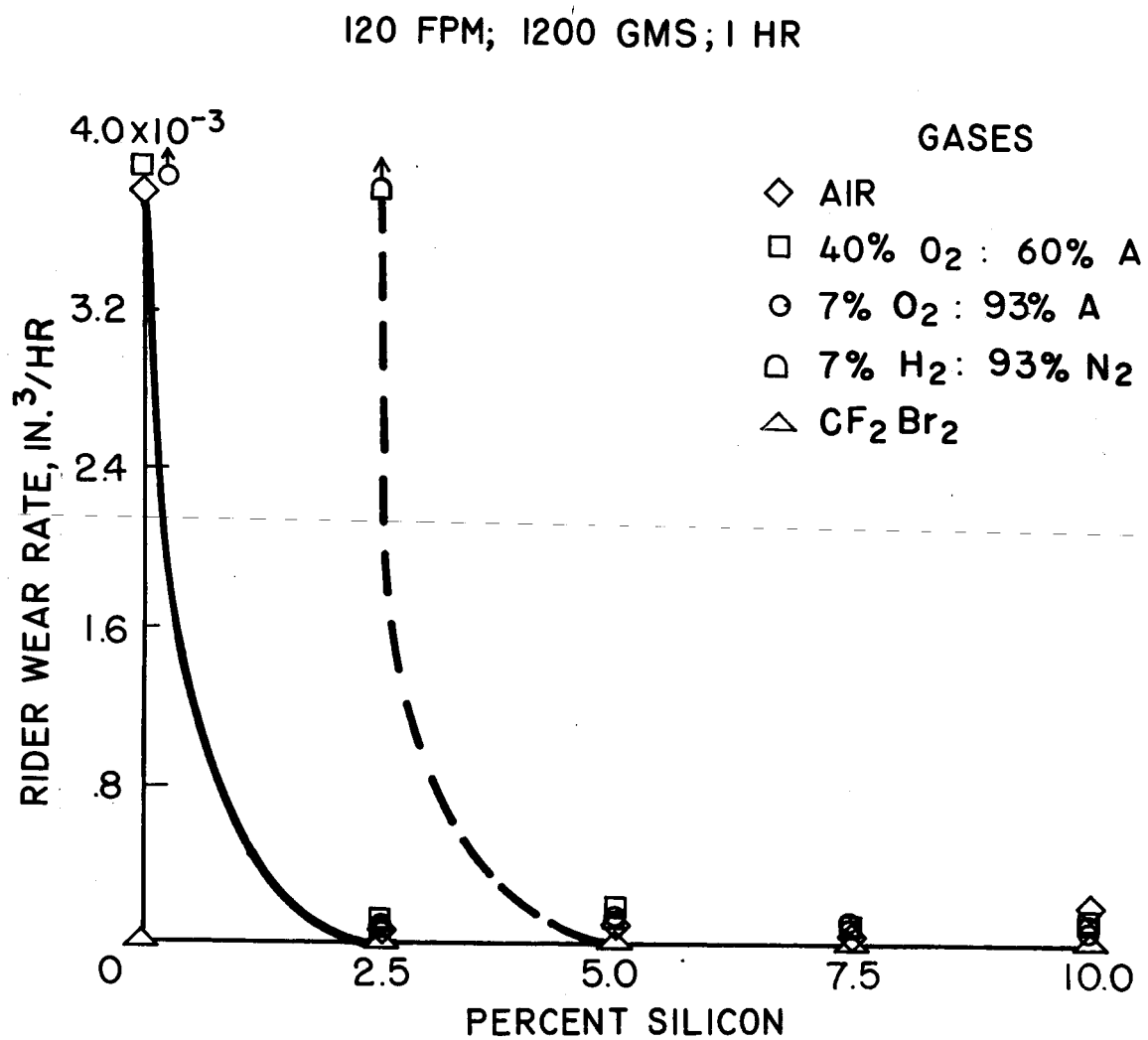
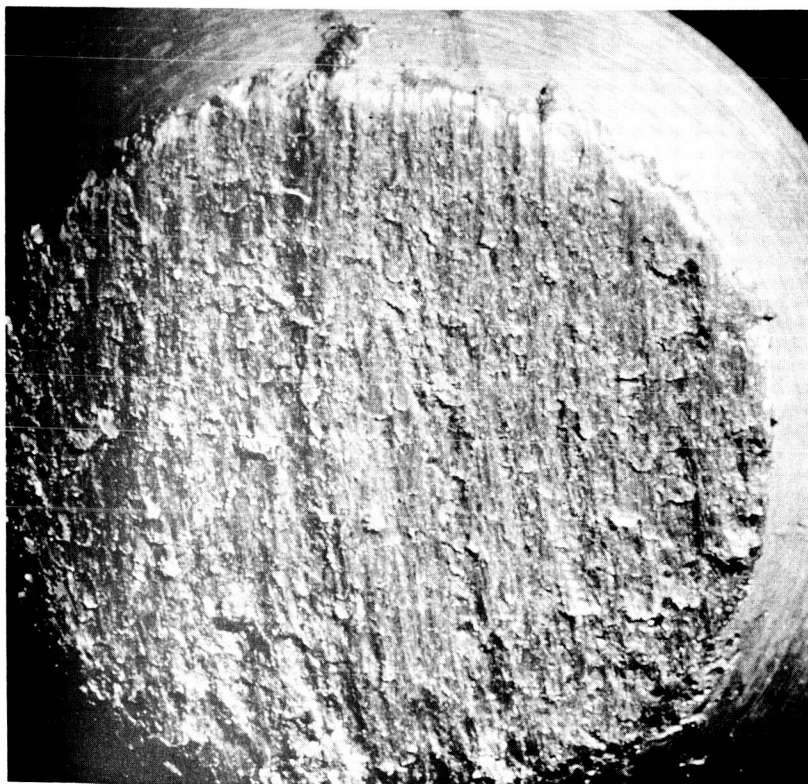
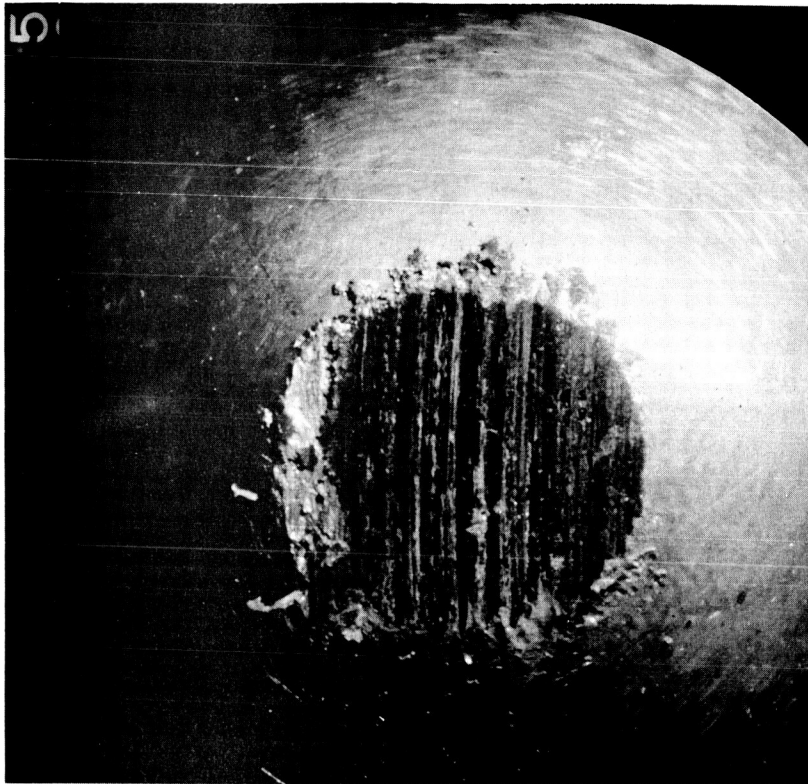


Figure 10.

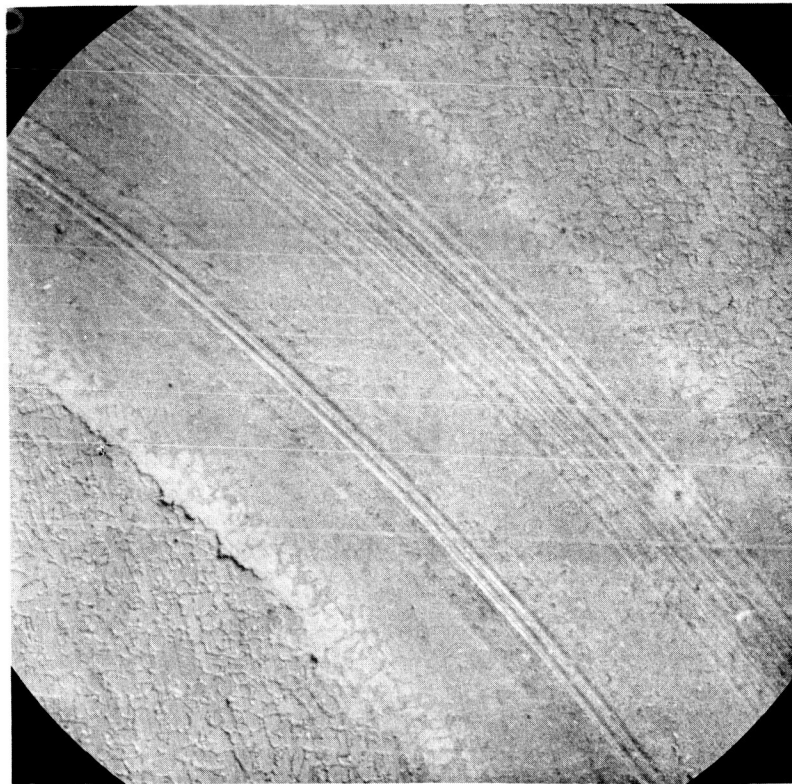


(A) L-NICKEL

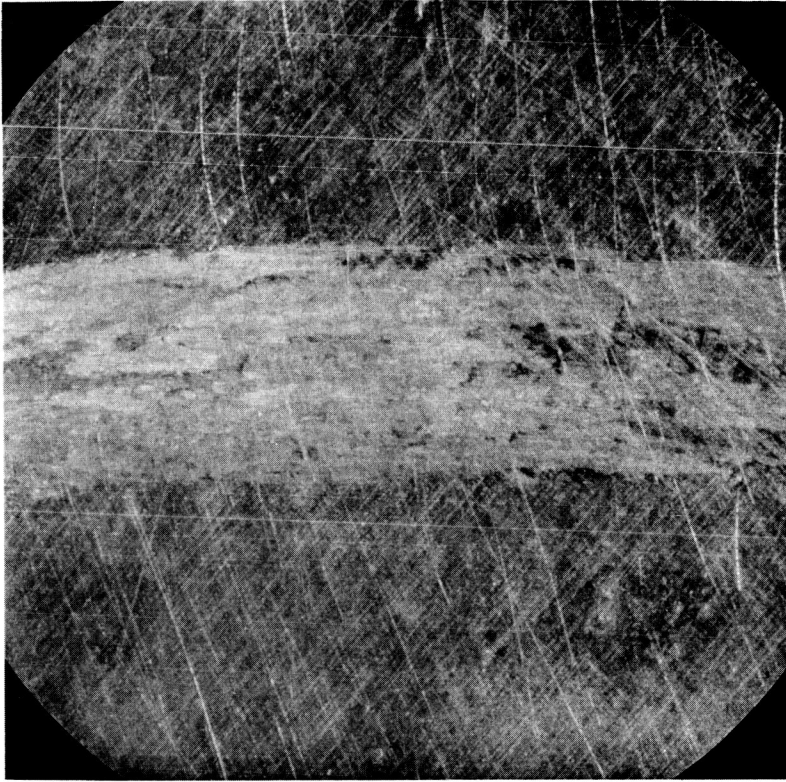


(B) 2.5 PERCENT SILICON-NICKEL

Figure 11.

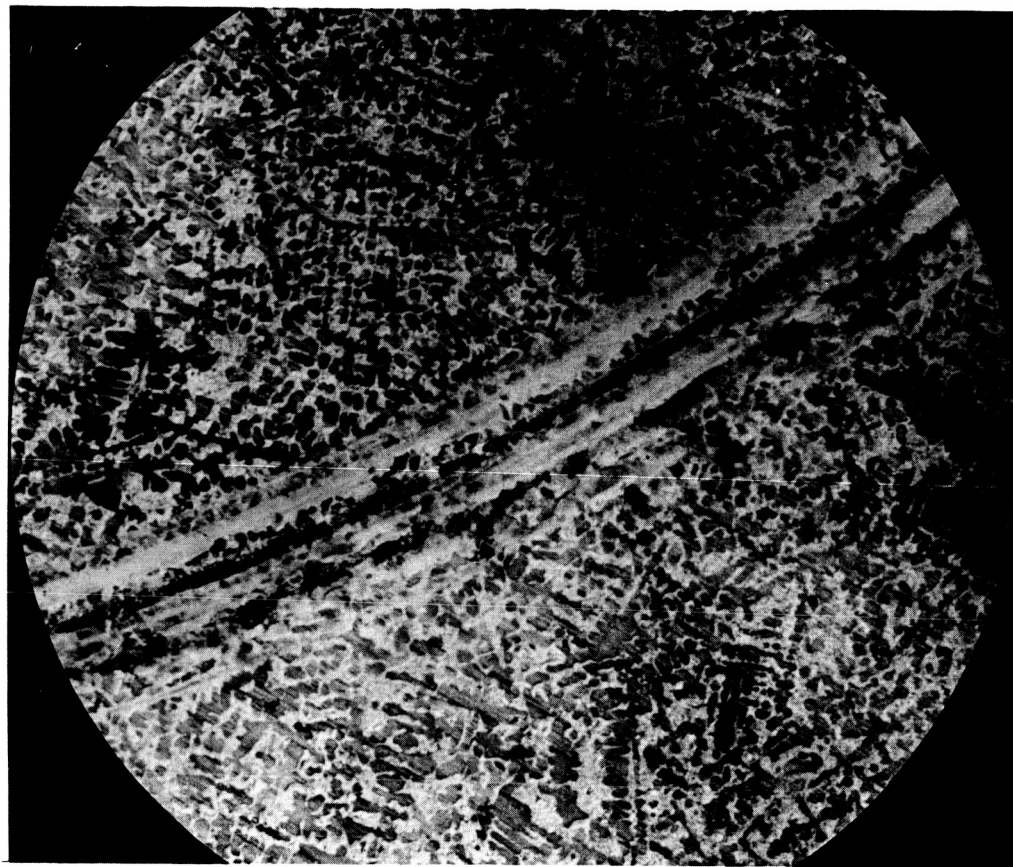


(A) AIR



(B) FORMING GAS

Figure 12.



(C) CF_2Br_2

Figure 12. - Concluded.